United States Patent [19]

Shiba et al.

[11] **3,915,713**

[45] **Oct. 28, 1975**

[54] **SILVER HALIDE PHOTOGRAPHIC EMULSION**

[75] Inventors: **Keisuke Shiba; Seiiti Kubodera; Haruo Takei; Atsuaki Arai; Mitsugu Tanaka; Takeo Sakai,** all of Minami-ashigara, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.,** Minami-ashigara, Japan

[22] Filed: **Nov. 2, 1973**

[21] Appl. No.: **412,518**

[30] **Foreign Application Priority Data**

Nov. 2, 1972 Japan 47-110074

[52] **U.S. Cl.** **96/107;** 96/66.3; 96/95; 96/109

[51] **Int. Cl.²** **G03C 1/28**

[58] **Field of Search** 96/107, 109, 66.3, 95

[56] **References Cited**

UNITED STATES PATENTS

3,320,068	5/1967	Bardorff et al.	96/107
3,321,312	5/1967	Bardorff et al.	96/109
3,615,528	10/1971	Huckstadt et al.	96/66.3
3,632,340	1/1972	Illingsworth	96/33
3,707,376	12/1972	Van Stappen et al.	96/107

Primary Examiner—Norman G. Torchin
Assistant Examiner—Edward C. Kimlin
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

A silver halide photographic emulsion having an improved initial speed of development, especially in an infectious development process, and capable of producing a picture image with high edge gradient, which contains as the silver halide at least 40 mol % of silver chloride, with the silver halide having an average particle size of not more than 0.8 micron, and containing as a combination of the following compounds:

1. a polyalkylene oxide compound and
2. an organic compound having at least one hydroxyl group and at least one amino group consisting of a tertiary nitrogen atom.

45 Claims, 3 Drawing Figures

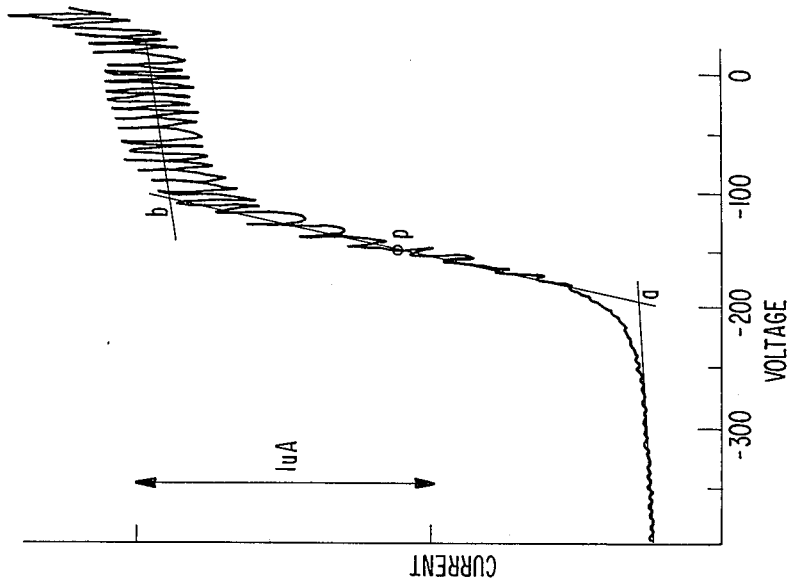


FIG 3

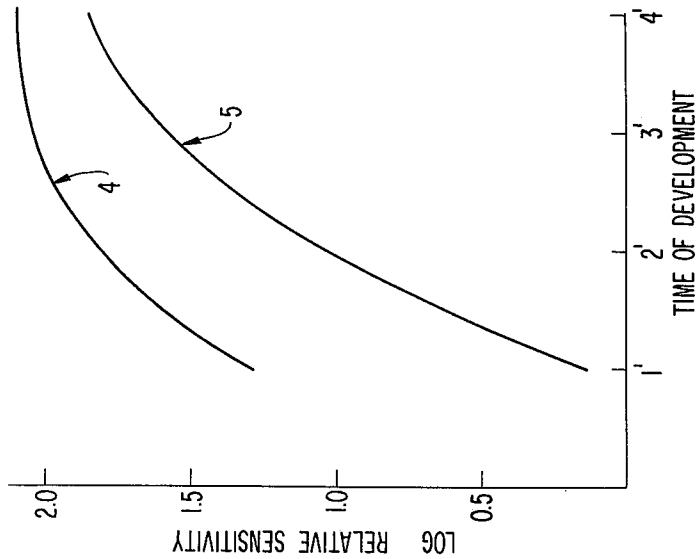


FIG 2

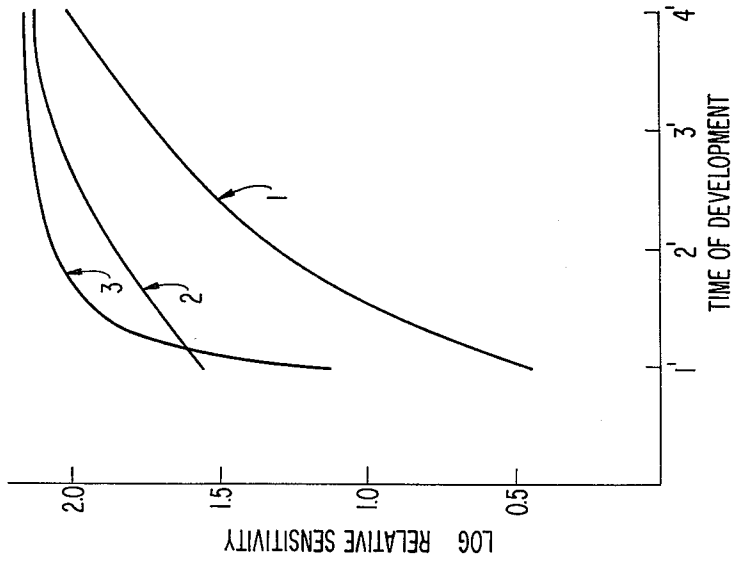


FIG 1

SILVER HALIDE PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an improved silver halide photographic emulsion. More particularly, the invention relates to a silver halide photographic emulsion suitably used in a lith type photosensitive material having an increased sensitivity in the initial stages of an infectious development process and having increased edge gradient of the picture image resulting therefrom.

The term "edge gradient" as used herein refers to the degree or rate of the change in the optical density in relation to the vertical direction to the edge formed as a contact line between the darkened and undarkened parts of the developed photographic picture image. In general, it can be said that the higher the edge gradient, the clearer or sharper the picture image is.

2. Description of the Prior Art

A photosensitive material having an increased edge gradient is advantageously used, for example, as a lith type photosensitive material used in photoprinting or phototypesetting where cross-line images are formed with the use of a glass screen or a contact screen. In this type of photosensitive material, it is known to ensure simple and easy handling, that matters such as increasing the edge gradient, enhancing the sensitivity, minimizing the granularity, and accelerating the rate of developing speed are required. In addition, when development is carried out under severe conditions, it is known to retard the fatigue of the developing liquid, i.e., to increase the tolerance, etc., to minimize the degradation of the picture quality.

In order to obtain a picture image having a high edge gradient, a lith type photosensitive material for use in phototypesetting is usually developed using an infectious development process.

The "infectious development process" generally comprises developing with a developer containing hydroquinone as the major developing agent together with a very minor amount of a sulfite, an inorganic alkali salt or an organic amine, and using a pH as high as **9.5** or higher.

Development using an infectious developer inevitably is accompanied by the disadvantages of poor sensitivity, slow initial developing speed, non-uniformity in the picture image quality obtained after every developing procedure and poor granularity of the picture image etc., as compared with another type of developer in which a developing agent capable of imparting superadditivity has been combined with the major developing agent such as is seen in the conventionally employed metolhydroquinone type developer, metol-pyrazolidone type developing agent, etc. In addition, a silver halide emulsion containing a polyoxyalkylene oxide derivative is used as a lith type photo-sensitive material to strengthen the infectious development and to suppress non-infectious developability. However, the addition of such a polyalkylene oxide derivative greatly decreases the initial developing speed. In other words, a prolonged developing time is required for such emulsions to ensure infectious development with effectively high contrast. Once the infectious developing has started, the polyoxyalkylene oxide derivative strengthens the development outstandingly while providing high contrast, but a much too long period of time for the initiation of the infectious developing is required permitting, in the meantime, gradiations of extremely low contrast and high contrast to coexist thereby aggravating "foot cutting".

Moreover, spectral sensitization is often applied to lith type photosensitive materials in order to increase the sensitivity in a specific wave length region. However, most of the sensitizing dyes tend to slow down the initial speed of the infectious development with an appreciable degradation of "foot cutting".

When the so-called infectious development is used for the development of a lith type photosensitive material, many more disadvantages, which seriously affect the developing performance, arise due to the presence of various additives from the silver halide emulsion and due to substances which undergo chemical change during the developing procedure, than when conventional non-infectious type developers are employed.

Additives which have been conventionally used effectively in a black-and-white non-infectious type developer, e.g., **D-16, D-19,** and **D-72** (these developers and their compositions are well-known in the art) are not also always similarly effective for the infectious developer. They rather invite a decrease in the edge gradient due to the disappearance of infectious developability, generate fog and promote fatigue of the developer and like disadvantageous influences.

Accordingly, an object of the present invention is to provide a photographic emulsion in which all of the defects described hereinabove have been eliminated or reduced remarkably. More particularly, an object of the present invention is to provide a photographic emulsion which satisfies the following criteria of: **(1)** increasing the initial developing speed, **(2)** obtaining high sensitivity with possible a minimum developing period, **(3)** obtaining a high edge gradient with possible a minimum developing period, **(4)** retaining excellent granularity while retaining high sensitivity, **(5)** maintaining a high edge gradient after a high degree of development, and **(6)** retaining satisfactory tolerance.

Another object of this invention is to provide a method for the preparation of silver halide emulsions which satisfies to a large extent the above requirements simultaneously.

These and other objects of the present invention will be understood by referring to the following detailed disclosure and working examples thereof.

SUMMARY OF THE INVENTION

It has now been found that the above objects can be accomplished with a silver halide photographic emulsion containing a silver halide comprising at least **40** mol % of silver chloride and in which the average particle diameter of the silver halide particles is not greater than **0.8** micron and further containing therein a combination of; **(1)** a polyalkylene oxide compound and **(2)** and an organic compound having at least one hydroxyl group and at least one amino group consisting of a tertiary nitrogen atom (especially one capable of promoting infectious development).

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

FIGS. **1** and **2** are each diagrams indicating the relationship between the development period and the relative sensitivity. These figures designate the speed of the development relatively.

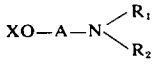
FIG. 3 indicates voltage-current curve (polarograph) from which the oxidation potential (E_{ox}) is determined. Points a and b represent the points at which the three line segments intersect, each of the lines extending through the connected middle point of the curves in the ordinate direction indicating current value.

DETAILED DESCRIPTION OF THE INVENTION

In more detail, the organic compound having at least one hydroxyl group and at least one amino group with a tertiary nitrogen atom, should have a specific reducing activity against the oxidation product (i.e., semiquinone) formed during the development the main developing compound (e.g., hydroquinones).

This specific compound is an aromatic compound or a heterocyclic compound (of these two, an aromatic compound is preferred) having an oxidation potential (to be defined hereinafter) (E_{ox}) of from about **0** millivolt to about **−200** millivolt, preferably up to **−160** millivolt, or precursors (regardless of their oxidation potential) of these compounds. Especially preferred compounds are those represented by the following general formula (**1**):

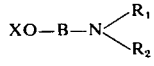
GENERAL FORMULA I



(I)

wherein A represents a bivalent aromatic or heterocyclic group (e.g., a benzene group, a naphthalene group, a pyrimidine group, a triazine group), and A can be substituted with substituent groups so as to satisfy the value of E_{ox} required (e.g., alkyl (e.g., methyl, ethyl, propyl, butyl, etc.), alkoxy (e.g., methoxy, ethoxy, etc.), hydroxy, halogen (e.g., chlorine, bromine, etc.), alkoxycarbonyl (e.g., methoxy carbonyl, ethoxycarbonyl, etc.), quaternary aminoalkyl, aralkyl (e.g., benzyl, phenethyl, etc.), aryl (e.g., phenyl, etc.), etc.); R_1 and R_2 each represents a group which is necessary to form a tertiary amino group with the nitrogen atom, and is preferably an alkyl group (e.g., a methyl, ethyl, butyl, hydroxyalkyl such as hydroxyethyl, aminoalkyl such as trimethyl aminoethyl group, etc.), an alkenyl group (e.g., an allyl group), an aralkyl group (e.g., a benzyl, p-hydroxyphenyl-substituted alkyl group, etc.), or an aryl group (e.g., a phenyl, hydroxyphenyl, acetoxyphenyl, alkoxycarbonyloxyphenyl group, etc.), and R_1 and R_2 can combine together to form a closed (saturated or unsaturated) ring; X represents either hydrogen, or a group capable of being dissociated therefrom with an inorganic or organic base (e.g., an acetyl, benzoyl and like acyl groups, an acetoxy and like acyloxy groups. The compound to which these dissociatable groups are attached is defined as a "precursor" which under the development conditions releases its dissociable group with the compound behaving as if X were originally a hydrogen atom.

The compound represented by the general formula (**1**) usually exists in a stable state as the form of a "Lewis acid-base salt" with an inorganic or organic acid (e.g., hydrochloride acid, sulfuric acid, nitric acid, sulfurous acid, oxalic acid, p-methylbenzene sulfonate and sulfuric acid etc.), so that it can be employed in such a stabilized form. Especially preferred compounds of the general formula (I) above are those having the general formula (I-*a*)

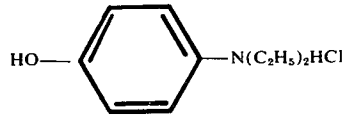


(I-a)

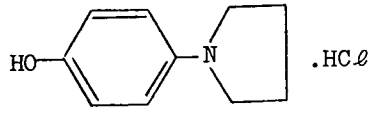
wherein B represents a bivalent benzene type aromatic ring group, and X, R_1 and R_2 each is as defined with respect to the foregoing general formula (I).

Typical compounds represented by the general formula (1) and which can be employed in this invention are exemplified by the following compounds. However, the invention is not limited to these compounds only, and other compounds which have been described in German Pat. Laid-open Specification Nos. 2,153,632; 2,153,633, 2,153,571; 2,153,572, 2,161,431 etc. can be employed.

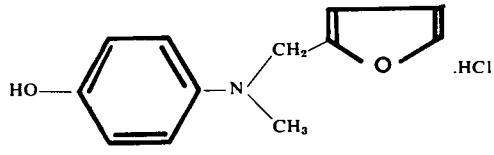
(I-a)



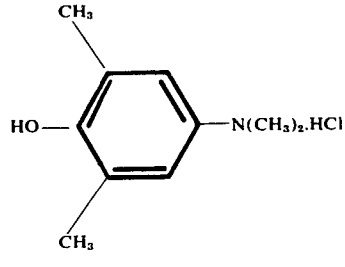
(I-b)



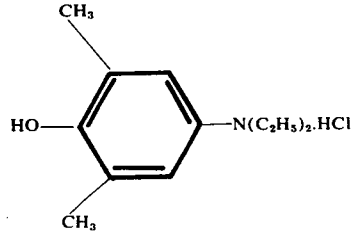
(I-c)



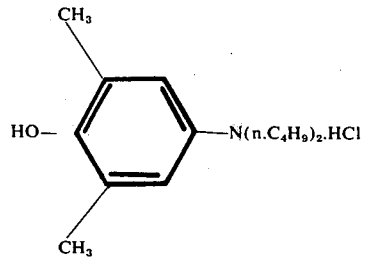
(I-d)



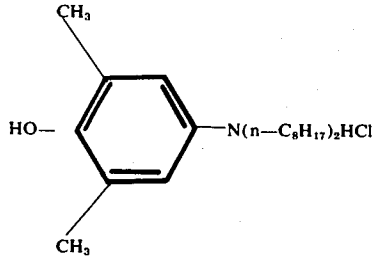
(I-f)



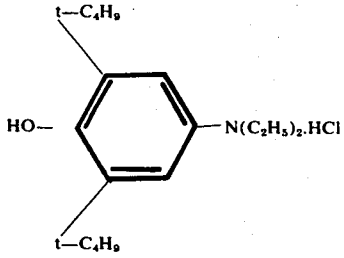
(I-g)



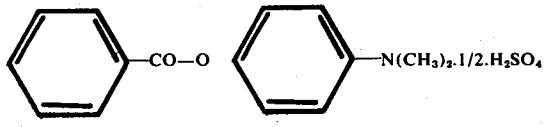
(I-h)



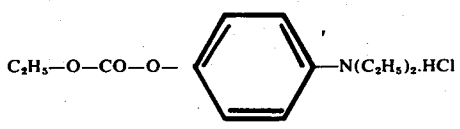
(I-i)



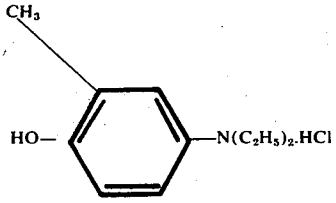
(I-j)



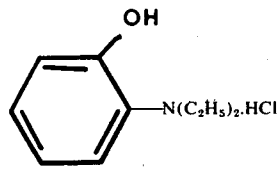
(I-k)



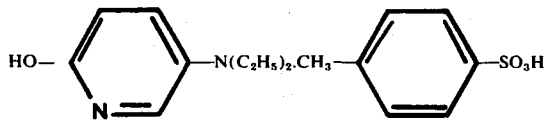
(I-l)



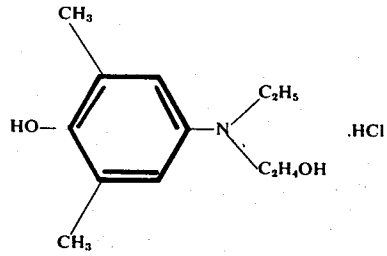
(I-m)



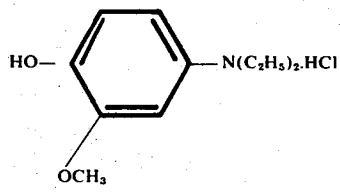
(I-n)



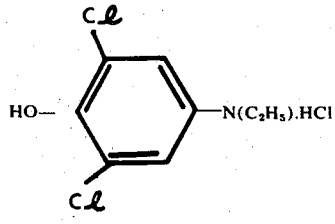
(I-o)



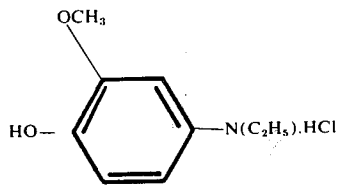
(I-p)



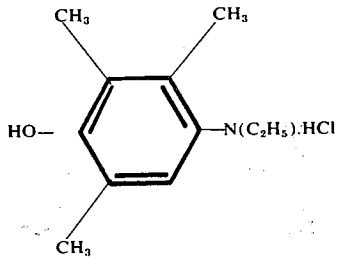
(I-q)



(I-r)



(I-s)



The compounds shown by (I-*j*) and (I-*k*) are examples of "precursor" compounds.

The process of development is understood as an oxidation-reduction reaction process between the silver halide and the developing compound.

Of the above-described compounds of this invention used as an element of the emulsion of this invention, the most desirable compounds for achieving the objects of this invention have the specific oxidation potental (E_{ox}) as set forth previously.

The value of the oxidation potential (E_{ox}) can be readily determined by voltametry as described hereinafter.

Firstly, a Britton-Robinson's buffer solution adjusted to a pH of 11.0 is prepared by mixing 825cc of a solution of sodium hydroxide (0.20N) with 1 liter of the solution containing dissolved therein 39.2g of orthophosphoric acid, 24.0g of glacial acetic acid and 24.7g of boric acid (the solution showed a pH value of 11.0 at 25°C). The buffer solution thus prepared is then bubbled with nitrogen gas to completely replace the air, after which the samples to be measured are dissolved therein to prepare a $1\times10^{+3}$ mol solution of each sample. After placing a dropping mercury electrode in this solution, a voltage-current curve is plotted at 25°C using a saturated calomel electrode (SCE) as a reference electrode. The oxidation potential (E_{ox}) is determined from this curve by determining a half-wave potential therefrom according to the usually employed graphical method.

A series of the measured values sometimes gives rise to a deviation of approximately 100 millivolts depending upon the effect of the salt of the compound, although the compensations in the liquid-liquid contact potential, electric resistance, etc. specific to the apparatus are occasionally carried out by suitable adjustments in the electric circuits of the tripolar type polarography apparatus. However, in case of measuring only one compound, for instance, in case of measurement with hydroquinone, the reproducibility of the value of the oxidation potential can be obtained by comparing and adjusting the measured value while taking −150±2 millivolt as the standard.

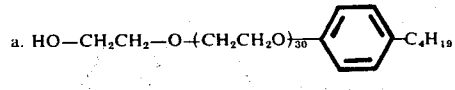
The term oxidation potential means the electric potential at which the sample is oxidized at the anode. The methods for the measurement of the oxidation potential are described in a variety of publications such as P. Delahay, *New Instrumental Methods in Electrochemistry*, Interscience Publishers, 1954; I. M. Kolthoft and J. J. Lingane, *Polarography*, Second Edition, Interscience Publishers, 1952; L. Meites, *Polarographic Techniques*, Second Edition, Interscience Publishers, 1965, etc.

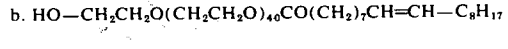
The oxidation potential as used throughout the specification refers to the one regarding the form in which a proton has been dissociated from the organic compound, and therefore it is preferred that the measurement be carried out in a solution with a sufficiently high pH value. In this case, the measurement of the oxidation potential of the organic compound represented by the general formula (I) is desirably carried out within about one hour after the preparation of the alkaline solution, since the organic compound tends to undergo decomposition, for instance, deamination, in an aqueous solution having a pH in excess of about 10.

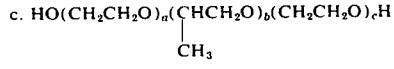
The polyalkylene oxide compound which can be used in this invention is a compound having therein at least a partial structure of or units of a polyalkylene oxide which serves for increasing the infectious developing effect with the use of a silver halide photographic emulsion, such as those described, for example, in U.S. Pat. Nos. 2,400,532; 3,294,537; 3,294,540; 3,516,830; 3,567,458 and 3,345,175;(the latter three corresponding to French Pat. Nos. 1,491,805; 1,596,673; Japanese Pat. Publication No. 23466/**1965** respectively), etc.

Examples of suitable polyalkylene oxide compounds include an addition polymer of ethylene oxide, of propylene oxide and like alkylene oxides with a compound such as water, aliphatic alcohols, aromatic alcohols, glycols, aliphatic acids, organic amines and a dehydration compound of hexitol, a condensate of a polyalkylene oxide with one of the above group of the compounds, or an inter-block copolymer of various different alkylene oxides (e.g., ethylene oxide and propylene oxide).

The polyalkylene oxide compounds used in this invention has a molecular weight ranging from about 500 to 25,000, preferably from 1,000 to 20,000, and includes, for example, the following compounds:

a. 

b. 

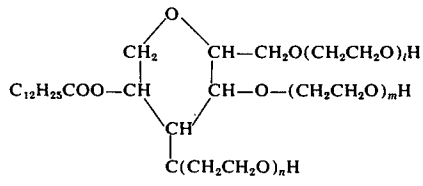
c. 

(wherein *a*, *b* and *c* are integers with *b* being an integer of 14 to 55 and with *a*+*c* being an integer of 4 to 210)

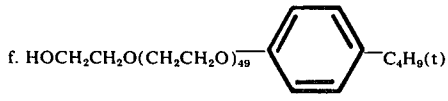
A number of various commercial products satisfy the above requirements with a variety of values for *a*, *b*, and *c* and with a variety of molecular weights. These products are presently available under the trade names of Pluronic L-44, L-61, L-62, L-64, L-68, L-81, P-65,

P-75 and F-88 (produced by the Wyandotte Chemical Co., respectively). For instance, L-68 has a molecular weight of 8750 with b=32, and $a+c$=159; P-75 has a molecular weight of 4100, with b=37, and $a+c$=51; F-88 has a molecular weight of 1,1250, with b=41, and $a+c$=204)

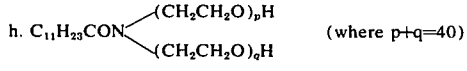
d. $HO-CH_2CH_2O(CH_2CH_2O)_{50}CH_2CH_2OH$



(where $l+m+n$ is about 20)



g. $C_{17}H_{35}COO(CH_2CH_2O)_{30}H$



(where p+q=40)

The silver halide emulsion used in this invention contains particles of silver chloride, silver bromide, silver iodide or mixtures, thereof and preferably consists of at least 40 mol % of silver chloride and less than 5 mol % of silver iodide or silver bromide. The silver halide particles used in this invention can have a uniformly distributed halogen composition inside the particles or the particle surface can have a different composition from that of the interior. The technique of the present invention can be applied not only to conventionally employed surface sensitive type negative emulsions but also to internal latent image type emulsions, direct positive type emulsions having a chemically fogged surface, and to other emulsions such as those prepared in accordance with the processes described, for instance, in U.S. Pat. Nos. 2,592,250; 2,996,382; 3,607,278 and 3,367,778; etc.

If the average diameter of the silver halide particle is higher than 0.8 microns, the granularity of the image obtained after infectious development will become much coarser than that obtained after ordinary non-infectious type developing.

The average diameter of the silver halide particle is determined according to conventional methods.

In greater detail, these methods of particle size determination are described in Triuelli and Smith, *Photographic Journal*, Vol.79, pages 330–380(1939); Trivelli, Righter and Sheppard, *Photographic Journal*, Vol.62, Pages 407–410(1922); P. F. Utt and K. F. Leverington, "The Determination of Silver Halide Crystal Distribution in Photographic Emulsion with the Zeis-Endter Particle Size Analyser", **1966** Particle Size Analysis Conference Report, pages 45–55, (published by Soc. Anal. Chem.) etc.

The photographic emulsion used in this invention can be sensitized using conventional techniques now well-known in the art, such as those described in C. E. K. Mees and T. H. James, *The Theory of the Photographic Process*, Second and Third Editions, including, for example, sulfur sensitization (as disclosed in U.S. Pat. Nos. 1,574,944; 2,378,947; 2,440,206; 2,410,689; 3,189,458; 3,415,649, etc.), reduction sensitization (as disclosed in U.S. Pat. Nos. 2,518,698; 2,419,974; 2,983,610; etc.), sensitizing with the use of noble metal ions (e.g., gold compounds, platinum compounds, etc. as disclosed in U.S. Pat. Nos. 2,540,085; 2,597,856; 2,597,915; 2,399,083, etc.), other metal ions other than silver such as metal ions of the Group VIII metals of the Periodic Table and Group II metal ions.

Typical examples of chemical sensitizers include thiourea, sodium thiosulfate, cystine and the like sulfur-containing sensitizers; potassium chloroaurate, aurous thiosulfate, potassium chloropalladate, and the like noble metal sensitizers; tin chloride, phenyl hydrazine, reductone and the like reducing sensitizers, etc.

Other sensitizers such as polyoxyethylene compounds (as disclosed in U.S. Pat. No. 2,716,062), polyoxypropylene compounds having an oxonium or ammonium group (as disclosed in U.S. Pat. Nos. 2,271,623; 2,288,226; and 2,334,864) can also be included.

In addition, high contrast (high gradation), stabilization, fog inhibition or supersensitization, etc. can be applied if desired.

Suitable examples thereof are antifoggants such as nitrobenzazoles, e.g., nitrobenzimidazole as disclosed in British Pat. No. 403,789, platinate salts, e.g., ammonium chloroplatinate, as disclosed in U.S. Pat. Nos. 2,566,263; and 2,566,245, etc., stabilizers such as 4-hydroxy-6-methyl-1, 3,3a,7-tetrazaindene, thiazolium salts as disclosed in U.S. Pat. Nos. 2,131,038 and 2,694,716, azaindenes, e.g., 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as disclosed in U.S. Pat. Nos. 2,886,437 and 2,444,605, urazoles as disclosed in U.S. Pat. No. 3,287,135, sulfocatechols as disclosed in U.S. Pat. No. 3,236,652, oximes, mercaptotetrazoles as disclosed in U.S. Pat. Nos. 2,403,927, **3,266,897,** and 3,397,987, nitrons, polyvalent metal salts as disclosed in U.S. Pat. No. 2,839,405, thiuronium salts as disclosed in U.S. Pat. 3,220,839, and salts of metals such as palladium, platinum and gold as disclosed in U.S. Pat. Nos. 2,566,263 and 2,597,915.

The photographic emulsion which can be used in this invention can contain as its protective colloid gelatin and acylated gelatin derivatives such as phthalated or malonated gelatin, cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose; hydrophilic polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide, polystyrene sulfonic acid, etc.; dimension stabilizing plasticizers, polymer latices such polymethyl methacrylate, polybutyl methacrylate, and matting agents such as silicon dioxide, etc.

The photographic emulsion which can be used in this invention can further contain developing accelerators such as onium compound, hydroquinone derivatives, 3-pyrazolidone derivatives and cationic surface active agents; stabilizers which are used in conventional photosensitive materials such as 4-hydroxy-1,3,3a,7-tetrazaindene derivatives; fog inhibitors such as mercaptotetrazol and lipoic acid; hardeners including inorganic compounds and organic compounds such as formaldehyde, other aldehydes, chromalum, mucochloric acid, sodium-1-hydroxy-3,5-dichlorotriazine, glyoxal, dichloroacrolein, aziridine etc., surface active

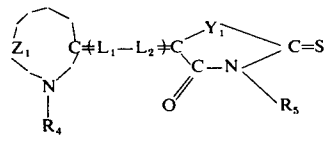
agents such as saponin, sodium alkyl benzenesulfonates, anionic surface active agents such as those described in U.S. Pat. No. 3,415,649; anionic, nonionic or amphoteric surface active agents conventionally used as coating aids such as the alkylarylsulfonates as disclosed in U.S. Pat. No. 2,600,831, amphoteric compounds as disclosed in U.S. Pat. No. 3,133,816; irradiation inhibiting dyes such as the merocyanine dyes, oxonol dyes, styryl dyes, naphthoquinone dyes, etc.

The layer of the photographic emulsion used in this invention can be provided with either on its upper or lower side at least one layer of a colloid which has been dyed to prevent halation or to exert a filtering activity.

The silver halide photographic emulsion can be spectrally sensitized using various methine dyes as disclosed in C. E. K. Mees *The Theory of the Photographic Process* Revised Ed. MacMillan; Frances M. Hamer *The Cyanine Dyes And Related Compounds*, Interscience Publishers, e.g., cyanine dyes, merocyanine dyes, hemicyanine dyes, complex merocyanine dyes, styryl dyes, neutrocyanine dyes, etc.

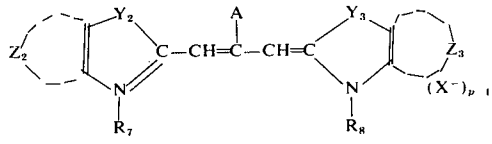
The use of sensitizing dyes represented by the following general formulae (II) or (III) are especially desirable;

GENERAL FORMULA II

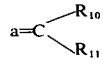


wherein Z_1 represents a group of atoms necessary for forming a heterocyclic ring such as a tetrazole ring, a pyrrolidine ring, a pyridine ring, a thiazole ring, a thiazoline ring, a selenazole ring, a selenazoline ring, an oxazole ring, an oxazoline ring, an imidazole ring, an imidazoline ring and an indolenine ring; L_1 and L_2 each represents a methine chain, for example, a methine chain, a methyl methine chain, an ethyl methine chain, a phenyl methine chain and 2-hydroxyethyl methine chain etc.; Y_1 represents an oxygen atom, a sulfur atom or a $=N-R_6$ group in which R_6 is an aliphatic group including a saturated aliphatic group and an unsaturated aliphatic group (e.g., an unsubstituted alkyl group and a substituted alkyl group wherein the alkyl moiety preferably has up to 5 carbon atoms) such as an alkyl group (e.g., methyl, ethyl and propyl groups), a cyanoalkyl group (e.g., cyanoethyl) an allyl group (e.g., vinyl methyl), a carboxyalkyl group such as a carboxymethyl group and a carboxyethyl group, an aminoalkyl group such as a dimethylaminoethyl group, an aralkyl group such as p-carboxyphenylmethyl group, a hydroxyalkyl group such as a hydroxyethyl group, an aryl group such as a phenyl group, a p-sulfophenyl group, etc.; n is an integer of 0 or 1; R_4 and R_5 are each an aliphatic group including a saturated aliphatic group and an unsaturated aliphatic group (e.g., an unsubstituted alkyl group and a substituted alkyl group wherein the alkyl moiety preferably has up to 5 carbon atoms), e.g., an alkyl group such as a methyl and ethyl group, a carboxyalkyl group (e.g., a carboxymethyl and carboxybutyl group), a sulfoalkyl group (e.g., sulfopropyl), an allyl group (e.g., vinylmethyl), an aminoalkyl group such as a morpholinoethyl group, an acetoxyalkyl group such as an acetoxypropyl group, an aralkyl group such as a benzyl group, an aryl group such as a phenyl, p-carboxyphenyl and tolyl group.

GENERAL FORMULA III



wherein A is a hydrogen atom or a lower alkyl group containing not more than 3 carbon atoms; Z_2 and Z_3 each represents a group of atoms necessary for forming a benzene type or a naphthalene type aromatic ring; Y_2 and Y_3 are each an oxygen atom, a sulfur atom, a selenium atom, a $=N-R_9$ group, in which R_9 is an aliphatic group including a saturated aliphatic group and an unsaturated aliphatic group (e.g., an unsubstituted alkyl group and a substituted alkyl group wherein the alkyl moiety preferably has up to 5 carbon atoms) an such as an alkyl group, e.g., a methyl, ethyl, isopropyl group etc., an allyl group (e.g., vinylmethyl), an acetoxyalkyl group (e.g., acetoxyethyl), a cyanoalkyl group such as cyanoethyl group, or



group, in which R_{10} and R_{11} are each an alkyl group such as methyl or ethyl. The above aromatic ring formed by Z_1 and Z_2 can be further substituted with an aryl group (e.g., phenyl, etc.), a halogen atom (e.g., chlorine, bromine, etc.), an alkyl group (e.g., methyl, ethyl, etc.), an alkoxycarbonyl group (e.g., methoxy carbonyl, ethoxy carbonyl), an alkoxy group (e.g., methoxy, ethoxy, propoxy, etc.), a trifluoromethyl group, an alkylsulfonyl group (e.g., methyl sulfonyl ethylsulfonyl, etc.). Eventually, the heterocyclic nuclei formed may include, for example, heterocyclic nuclei such as 5-phenyl-benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-methoxycarbonylbenzoxazole, 5-chlorobenzothiazole, 5-methoxybenzothiazole, 5-chloro-6-methylbenzothiazole, β-naphthothiazole, β,β′-naphthothiazole, 5-methylbenzoselenazole, benzoselenazole, 5,6-dichlorobenzimidazole, 5-trifluoromethylbenzimidazole, 5-chloro-6-methylsulfonylbenzimidazole, 5-methoxycarbonylbenzimidazole, naphthoimidazol-1,1′-dimethylindolenine, etc.

R_7 and R_8 each represents an alkyl group (e.g., an ethyl group, a propyl group etc.), a substituted alkyl group (e.g., a propenyl group, a hydroxyalkyl group such as a hydroxyethyl group, an amidoalkyl group such as an amidoethyl group, an aralkyl group such as a p-carboxyphenylmethyl group, a carboxyalkyl group such as a carboxymethyl, carboxy ethyl and carboxybutyl group, a sulfo group-containing alkyl group such as sulfopropyl group, a 3-sulfobutyl group, a 2-[2-(3-sulfopropoxy)-ethoxyethyl group, etc. In addition to the above, those substituents described in E. J. Poppe, *Zeitschrift für Wissenschaftliche Photographie* Vol. 63, pages 149–158 (1969) are also included. X^- represents an organic or inorganic anion generally used in a cyanine type dye such as a bromide ion, an iodide ion, a p-toluenesulfonic acid ion, a perchloric acid ion, etc. *p*

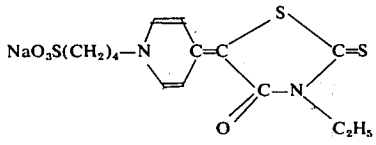
is 1 or 2, but when p is 1, the compound forms an intramolecular salt.

The methine dyes represented by the general formula (II) or (III) can be used alone or as a combination of two or more dyes selected from the group of the dyes represented by the general formula (II) or (III). Moreover, it is possible to combine the dye of the general formula (II) with dye of the general formula (III).

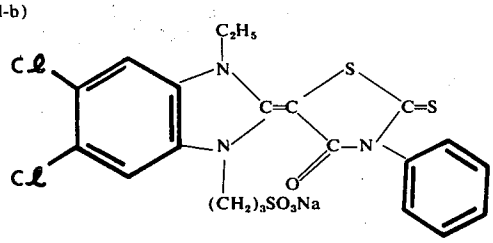
The dyes which can be used can be exemplified by the following compounds, the listing of which is not to be interpreted as limiting the scope of the invention.

General Formula II compounds:

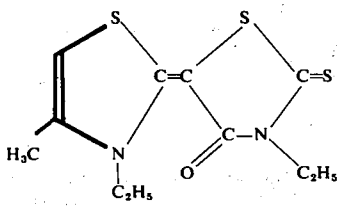
(II-a)



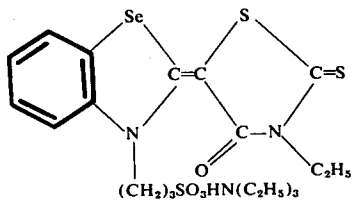
(II-b)



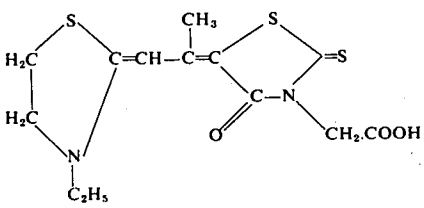
(II-c)



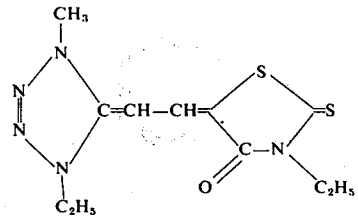
(II-d)



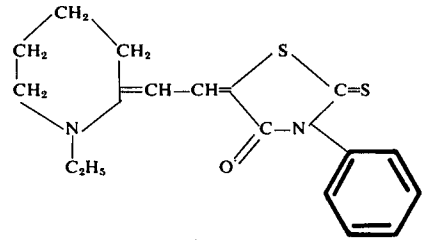
(II-e)



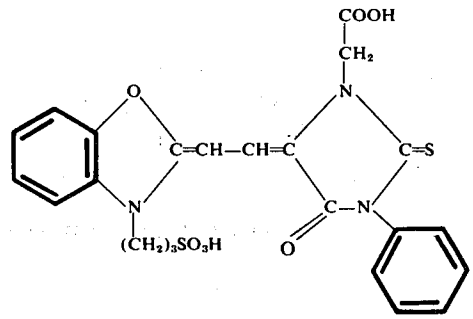
(II-f)



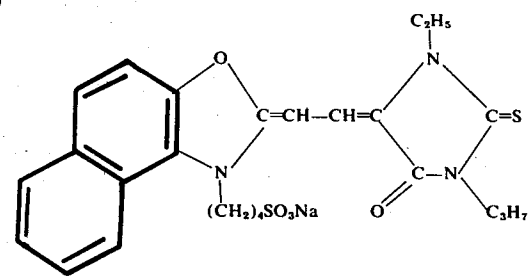
(II-g)



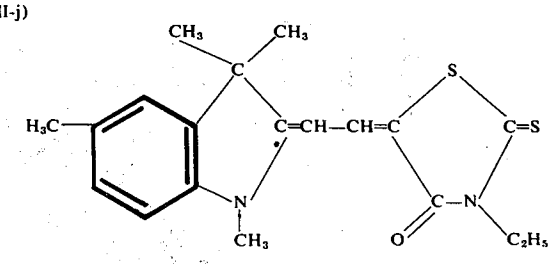
(II-h)



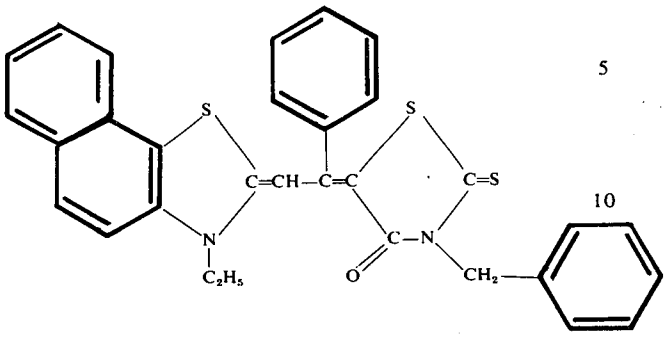
(II-i)



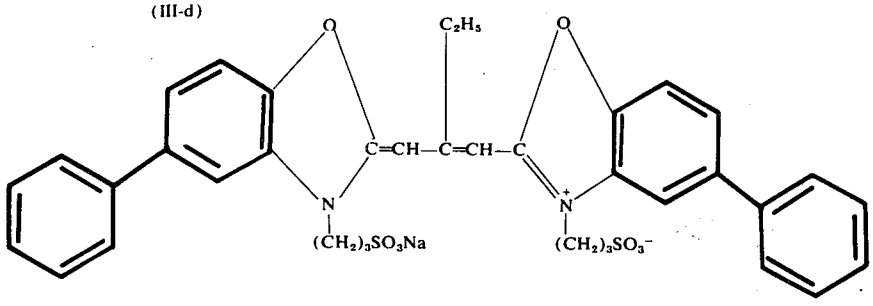
(II-j)



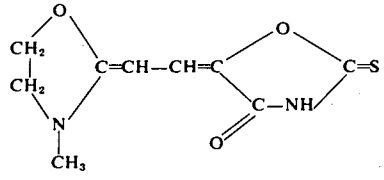
(II-k)



(III-d)

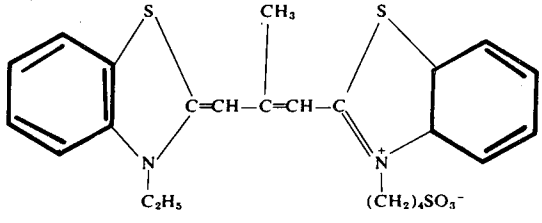


(II-l)

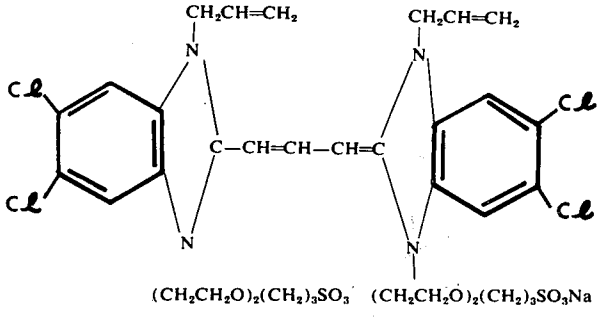


GENERAL FORMULA III COMPOUNDS:

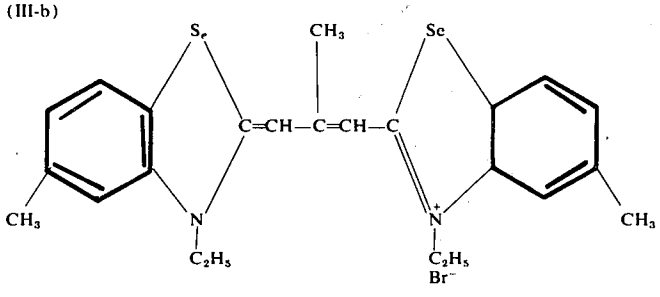
(III-a)



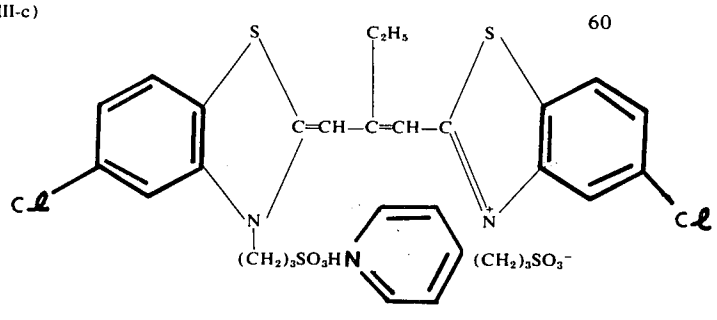
(III-e)



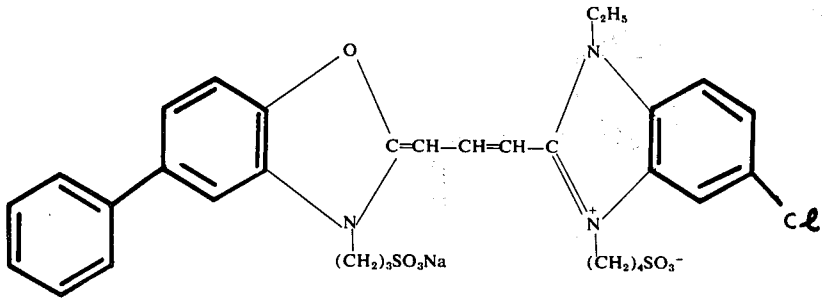
(III-b)



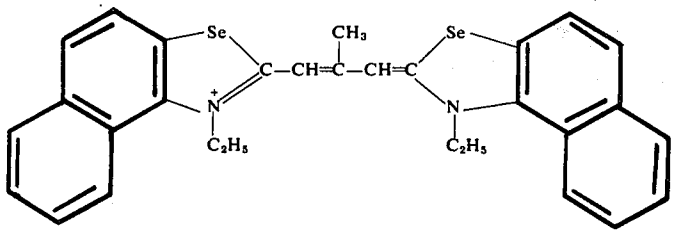
(III-c)



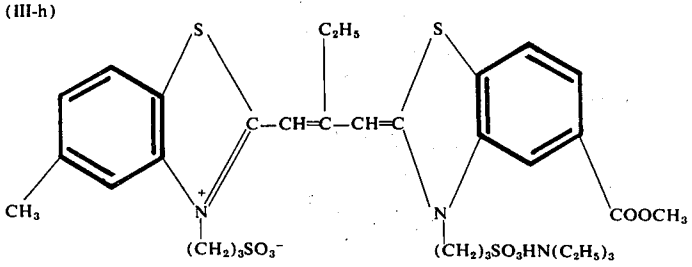
(III-f)



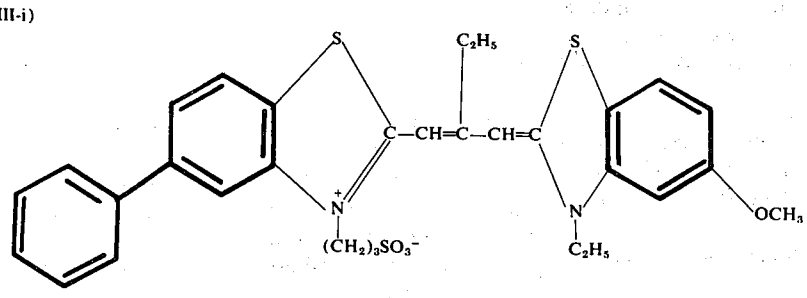
(III-g)



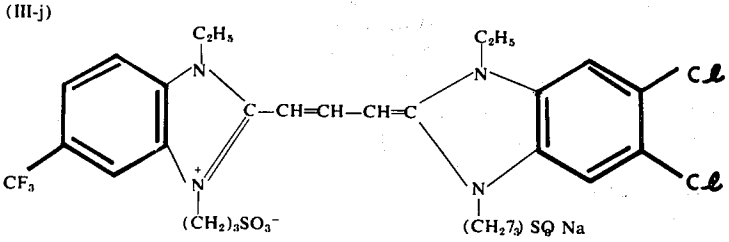
(III-h)



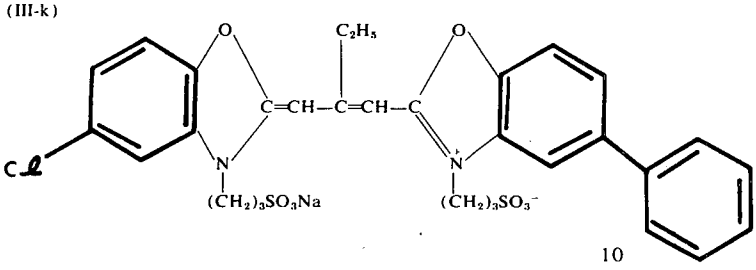
(III-i)



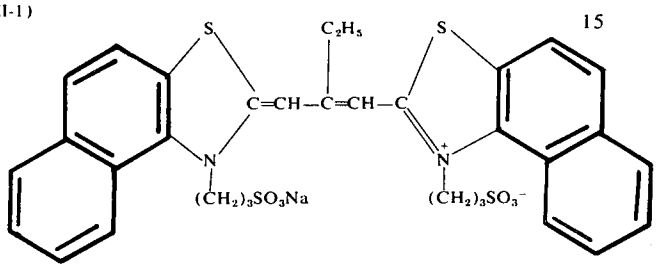
(III-j)



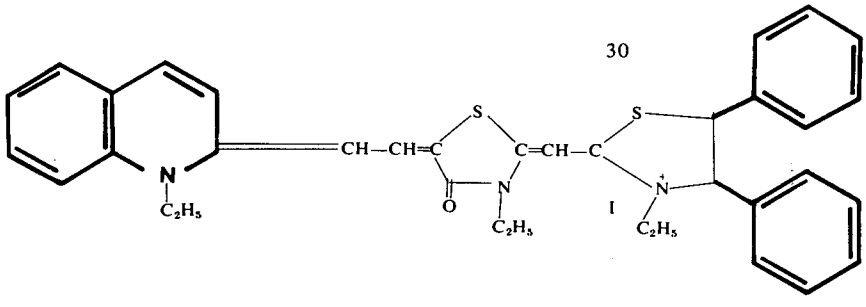
(III-k)



(III-l)



Examples of other compounds



The polyalkylene oxide compound which can be used in this invention is added in an amount sufficient to promote infectious development desirably in an amount of from 0.01 to 1 gram per mol of silver halide. The organic compound used as one indispensable element of this invention is preferably added in an amount of from 10^{-6} mole to 10^{-2} mole per mol of silver halide. The sensitizing dye which can be used in this invention is incorporated in a ssnsitizing amount, preferably in an amount of from 10^{-6} to 10^{-3} mol per mol of silver halide, which is sufficient to improve the sensitivity by usual sensitometry.

These additive compounds are added as solutions using solvents such as water or a suitable water-miscible solvent not adversely affecting the photographic properties of the silver halide emulsion such as alcohol (e.g., methanol, ethanol, methylcellusolve etc.), ketones (e.g., acetone, etc.).

The compound represented by the general formual (I) is preferably added as a neutral or acidic aqueous solution thereof.

These additive compounds can be incorporated using the techniques described in Japanese patent application No. 8231/**1970**, corresponding to U.S. patent application Ser. No. 111,501, filed Feb. 1, 1971 Japanese patent publication Nos. 27555/**1969**, **23389/1969**, **22948/1969** corresponding to U.S. Pat. Nos. 3,574,630; 3,585,195; 3,482,981 and 3,469,987 etc.

The finished emulsion is preferably kept at the pH below 6.8, especially below 6.5.

These additive compounds can be added directly to the emulsion itself, or added to at least one of the layers adjacent to the silver halide emulsion layer (such as a protective layer or an intermediate layer, an antihalation layer or other silver halide emulsion layers) through which the compounds eventually migrate and penetrate into the main silver halide emulsion layer.

The finished emulsion of the present invention can be applied to a suitable support material such as a polyethylene terephthalate film, a polystyrene film, a cellulose acetate film, a cellulose acetate butylate film, other plastic films, glass plates, etc.

The silver halide photosensitive material obtained in accordance with the present invention can be processed or treated in any conventional manner known in the art, for instance, in vat developing, automatic developing systems using rollers, belts and like mechanical transferring devices, or any other processes generally known in the art.

The development is carried out, for instance, using an infectious developer which is fundamentally consists of dihydroxybenzene (main developing agent), inorganic or organic bases, a minor amount of sulfite salts, and buffers containing sulfuric acid and a minor amount of sulfite salts.

The dihydroxybenzenes used as the main developing agent can suitably be selected from compounds well-known per se in photographic chemistry, and include, for example, hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethylhydroquinone, etc.

These compounds can be used either singly or as mixtures thereof as the developing agent and part of the amount used can be added to the silver halide emulsion.

The sulfite ion buffer is used in an effective amount so as to keep the concentration of the sulfite ions as low as possible, and includes an aldehyde-alkali metal bisulfite adduct, ketone-alkali metal bisulfite adduct such as acetone-alkali bisulfite adduct, and carbonyl bisulfuric acid amine condensate such as sodium bis-(2-hydroxyethyl)aminomethane sulfonate.

In order to render the developer liquid alkaline, preferably to a pH above 9.5, certain alkaline compounds including sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, sodium hydroxide, potassium hydroxide, organic bases such as 2-aminomethanol, 2,2'-iminodiethanol, triethanolamine, 2-ethylaminoethanol, etc. are added to the developer. These alkaline compounds can be added either alone or in combination.

The developer liquid can be further contain at least one of the following various additives well-known to those skilled in the art, such as, for example, benzothiazole, 1-phenyl-5-mercaptotetrazole and like organic fog inhibitors, polyalkylene oxides, amine compounds, onium compounds and organic solvent such as triethyleneglycol monoalkylether, etc.

The developer liquid can be prepared in the form of a powder of the developer components which has been widely used up to now, or in the form of a liquid containing the component which has been recently used with increasing interest to improve working efficiency and along with the increasingly widespread use of automatic developing apparatus.

The techniques in accordance with this invention can be applied in combination with other already known techniques such as those described in U.S. Pat. Nos. 3,252,101; 3,345,175; 3,220,844; 3,294,540; 3,447,459; 3,433,639; 3,294,537; 3,516,830; 3,518,085; 3,615,524; 3,567,458; 3,625,689; 3,600,174; 3,142,568; 3,325,286; and 3,346,368; British Pat. Nos. 1,098,748; and 1,163,724; and Ger,an Pat. Nos. 1,141,531; and 2,010,992; etc.

The present invention is illustrated in greater detail by the following examples. Unless otherwise indicated, all parts and percents are by weight.

EXAMPLE 1

A chemically ripened silver isdochlorobromide emulsion was prepared according to a conventional method. The bromide ion and the iodide ion contents were 17 mol % and 0.2 mol % respectively, and the amount of silver per kg of the emulsion was about 1.3 mol %.

The silver halide particles had an average diameter of about 0.6μ.

The emulsion (2.5Kg) was weighed into a pot and the vessel was heated to about 45°C to melt the contents. The contents were then spectrally sensitized by adding 100cc of 2×10^{-3} mol solution of the sensitizing dye (II-*e*) in methanol.

Successively, 100cc of a 1% aqueous solution of 2-methyl-4-hydroxy-1,3,3*a*,7-tetrazaindene was added as a stabilizer to the resulting solution. Thereafter the necessary additives were added according to the formulation as shown in Table 1 under stirring at about 45°C.

1° The addition of a compound selected from polyalkylene oxide compounds

2° The addition of a compound selected from the group of compounds represented by the genral formula (I).

To each emulsion thus obtained were added 50 cc of a 1% aqueous solution of sodium dodecylbenzene sulfonate and 50cc of a 2% solution of 6-hydroxy-2,4-dichloro-S-triazine sodium salt, and the resulting emulsion was applied to a glass plate and dried to form a coating having dried film thickness of 10μ.

After cutting into strips, the photosensitive material so obtained was wedge-exposed using a sensitometer having a color temperature of 5400°K. The thus exposed strip was developed using a conventional lith-type developer having the following composition at 20°C for 1,2,3 and 4 minutes respectively.

Composition of Developer I

Water	500 cc
Hydroquinone	15 g
Adduct of Formaldehyde with Sodium bisulfite	50 g
Potassium Carbonate	35 g
Triethanolamine	90 cc
Sodium Sulfite	2.5 g
Boric Acid	5.0 g
Potassium Bromide	2.0
Water to make	1 liter.

Composition of Fixing Liquid

Water	600 cc
Sodium Thiosulfate	360 g
Ammonium Sulfate	60 g
Anhydrous Sodium Sulfite	15 g
Glacial Acetic Acid	13.5 g
Boric Acid	7.5 g
Potassium Alum	15 g
Water to make	1 liter

The strips so processed was subject to densitometry so as to obtain characteristic curves, and the sensitivities thereof were calculated relatively taking the inertia point of the gradient scale obtained after infectious development as a standard.

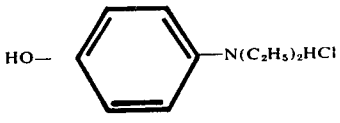
Table 1

No.	Polyalkyleneoxide (Conc.=0.5%) cc	Compound of General Formula (I) (Conc.=1×10^{-3}mol)cc	Result
1	—	—	—
2	(A) 100	—	FIG. 1 Curve 1
3	do. 100	(I-a) 40	do. Curve 2
4	do. 100	(I-f) 160	do. Curve 3
5	(A) 100	(I-d) 40	FIG. 2, Curve 4
6	(A) 100	(a) 40	do. Curve 5

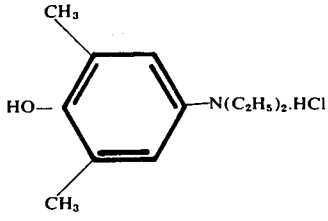
In the above Table 1;

A. was a polyethyleneoxide compound having approximately 50 ethyleneoxide units in to each oleylphenoxy group.

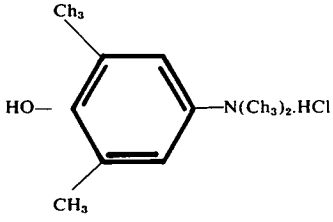
(I-a)



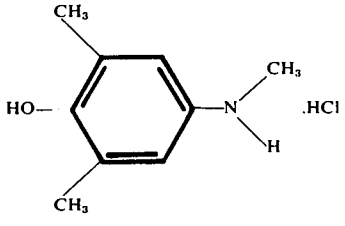
(I-f)



(I-d)



a. A compound for comparison



Runs No. 1, 2 and 6 were carried out for the purposes of comparison. The results of Run No. 5 clearly demonstrate the advantageous feature of the present invention in comparison with Run No. 6.

No infectious development took place.

EXAMPLE 2

The same original emulsion as was employed in Example 1 was weighed into a pot each in a 100g portion, heated at 45°C to melt it, then spectrally sensitized by adding 100cc of a 1×10^{-3} mol solution of the sensitizing dye (II-*f*) in methanol.

Using the procedure of Example 1, a polyalkyleneoxide compound, a compound represented by the general formula (I) and 6cc of 2% solution of mucochloric acid to give finished solution were added and the emulsion was thereafter applied to a polyethylene terephthalate film and dried to form a layer having a dried film thickness of about 6μ.

Sensitometry tests were carried out in a similar manner to Example 1, with the exception that the exposure was effected by closely contacting the film surface with a Gray Contact Screen manufactured by Dainippon Screen Manufacturing Co. (for positive use, 150 lines/inch). The relative sensitivity was indicated relatively with respect the exposed surface at which the optical density of the strips obtained reached the value of 1.50.

Composition of Developer Liquid II

Water	500 cc
Hydroquinone	15 g
Adduct of Formaldehyde with Sodium Bisulfite	50 g
Sodium Carbonate	80 g
Sodium Sulfite	25 g
Boric Acid	5.0 g
Potassium Bromide	2.0 g
Water to make	1 liter

Table 2

No.	Polyalkyleneoxide (Conc. %) cc			Compound of General Formula (1) (Conc. %) cc	Relative Sensitivity Developing Time 2 min.	3 min.	4 min.	Quality of Cross Line Points Period of Development Time 2 min.	3 min.	4 min.
7	(A)	0.5%	4.5cc	—	43	100	154	C	B	B
8			"	(1-a) 0.5% 1.5cc	162	191	210	A	B	B
9			"	(1-f) 0.5% 0.5cc	189	210	229	B	B	B
10			"	(1-1) 0.5% 0.5cc	110	145	179	B	A	B
11			"	(1-d) 0.5% 4.5cc	75	116	156	B	B	A
12	(B)	0.5%	5cc	—	44	110	158	C	B	B
13			"	(1-a) 0.5% 1.5cc	109	161	177	B	A	A
14	(C)	0.5%	2.5cc	—	25	88	151	C	B	A
15			"	(1-a) 0.5% 1.5cc	150	182	207	A	A	B
16	(D)	2%	5cc	—	88	138	172	B	C	C
17			"	(1-a) 0.5% 1.5cc	170	210	223	B	C	C
18	(E)	1%	4.5cc	—	45	106	160	C	B	A
19			"	(1-a) 0.5% 1.5cc	143	182	215	A	B	C

In Table 2:

B. A polyethylene oxide compound having approximately 30 ethylene oxide units to every oleylphenoxy group

C. Pluronic L-35, manufactured by the Wyandotte Chemical Co.

D. Polyoxyethylene sorbitan monooleate (n=40)

E. Polyoxyethylene laurate (n=40)

The cross line point quality was classified into 3 grades in the order of the sharpness of the cross line edge, i.e., A B C, by comparing with that of the standard sample (strips used for development for 3 minutes of Run No. 7). (Refer to the description of Japanese patent application Ser. No. 3037/**1962** corresponding to U.S. patent application Ser. No. 319815 filed Dec. 29, 1972)

EXAMPLE 3

A chemically ripened silver iodochlorobromide emulsion was prepared according to conventional method. The emulsion had a bromide ion content of 17 mol % and an iodine ion content of 1 mol%. The emulsion contained 80cc of a 4×10^{-3} mol solution of dye II-*a* in methanol and 50 cc of a 1×10^{-3} mol solution of dye II-*l* in methanol in each kg. to effect spectral sensitization. To the thus spectrally sensitized emulsion were added 500cc of a 1% solution of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene and a predetermined amount of a polyoxyethylene compound (A), then 100 cc of a 2% solution of 6-hydroxy-2,4-dichloro-S-triazine sodium salt was added to provide the finished emulsion.

On one hand, a colloidal composition to be used for making a protective layer was prepared, and thereafter the compound represented by the general formula (I) was admixed thereto.

Composition of Colloid for Protective Layer:

Gelatin	50 g
Water	1000 cc
Silicon Dioxide	0.2 g
Sodium 14-(p-nonylphenyl)-5,8,11,14-tetradecane-1-sulfonate (2%)	40 cc

A polyethylene terephthalate film base was firstly coated with the silver halide photosensitive layer in a dried film thickness of about 5μ, then the layer formed was further coated with the protective layer in a dried film thickness of about 1μ.

In a manner similar to Example 2, the resulting photosensitive film was exposed under a cross line screen and developed with the use of a roller type automatic developer and the developer liquid (I) at 27°C for 75, **105** and 135 seconds, respectively.

Table 3

Polyalkylene oxide Added cc		Compound of General Formula (I) Added to Emulsion (Conc. %) cc	Added to Protective Colloid Layer (conc. %) cc	Relative Sensitivity 75 sec.	105 sec.	135 sec.	Quality* of CrossLine Point 75 sec.	105 sec.	135 sec.
(A)	35	—	—	36	100	158	C	B	B
	"	(I-a) 0.5% 20	—	128	181	226	B	A	B
	"	(I-f) 0.5% 8	—	153	193	230	A	B	B
	"	(I-l) 0.5% 15	—	100	149	190	B	A	A
(A)	35	—	—	40	100	155	C	B	B
	"	—	(I-a) 0.5% 30	142	183	207	B	A	B
	"	—	(I-a) 0.5% 50	184	212	230	A	B	C

*Grades as previously described in Table 2

Any one of the compounds represented by the previously described general formulae (I), (II) or (III) can be used in place of the specific compounds employed in Examples 1, 2 and 3. The optimum quantity to be used can be easily determined according to testing methods known and employed ordinarily by those skilled in the art.

EXAMPLE 4

The value of oxidation potential (E_{ox}) used in this invention is determined according to the method as shown previously.

The potential current curve by taking hydroquinone as the standard material is shown in FIG. **3.**

The values of the E_{ox} of the compounds represented by the general formula (I) are given as follows:

(I-a)	−69	millivolt (mV)
(I-d)	−77	"
(I-f)	−105	"
(I-g)	−156	
(I-l)	−155	
(I-q)	−0	
(a)	−250	
Hydroquinone (standard)	−150±2	

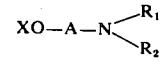
In FIG. **3,** the middle points of the curves between each of the upper limit and the lower limit in the ordinate direction ordinate which indicates current values are connected to give three extended line segments. The points at which the line segments cross are indicated as points *a* and *b*, respectively. The middle point *p* of the line segment formed between crosspoint *a* and crosspoint *b* is determined. The oxidation potential value (E_{ox}) of the present invention is then obtained as a voltage value corresponding to point *p*.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. In a lithographic silver halide photographic emulsion comprising at least 40 mol % of silver chloride and containing silver halide particles with the average particle diameter of not more than 0.8 micron, the improvement which comprises said silver halide photographic emulsion containing the combination of the following compounds:

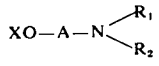
1. a polyalkylene oxide compound, and
2. an organic compound of the general formula (I)



wherein A represents a bivalent aromatic or heterocyclic group, R_1 and R_2 each represents a group which is necessary to form a tertiary amino group with the nitrogen atom, and R_1 and R_2 can combine together to form a ring; X represents either hydrogen, or a group capa-

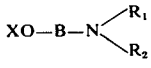
ble of being dissociated therefrom with an inorganic or organic base, or a precursor of said organic compound having the general formula (I), said compound of the general formula (I) having an oxidation potential ranging from 0 millivolt to −200 millivolt.

2. The photographic emulsion of claim **1**, in which said organic compound has the general formula (I)



wherein A represents a bivalent aromatic or heterocyclic group, R_1 and R_2 each represents a group which is necessary to form a tertiary amino group with the nitrogen atom, and R_1 and R_2 can combine together to form a ring; X represents either hydrogen, or a group capable of being dissociated therefrom with an inorganic or organic base, or a precursor of said organic compound having the general formula (I), said compound of the general formula (I) having an oxidation potential ranging from 0 millivolt to −200 millivolt.

3. The photographic emulsion of claim **1**, in which said organic compound has the following general formula (I-*a*)



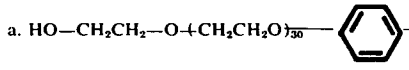
(I-a)

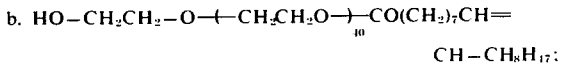
wherein B represents a bivalent benzene type aromatic ring group, and X, R_1 and R_2 each is as defined in claim **1**.

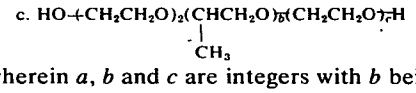
4. The photographic emulsion of claim **1**, wherein A is a unsubstituted or substituted benzene group, naphthalene group, pyrimidine group, or triazine group, said substituents being alkyl, alkoxy, hydroxy, halogen, alkoxycarbonyl, quaternary aminoalkyl, aralkyl or aryl groups; R_1 and R_2 each is an alkyl group, an alkenyl group, an aralkyl group or an aryl group or R_1 and R_2 can combine together to form a saturated or unsaturated ring; X represents a hydrogen atom, an acyl group, or an acyloxy group.

5. The photographic emulsion of claim **1**, wherein said polyalkylene oxide compound has a molecular weight ranging from about 500 to 25,000.

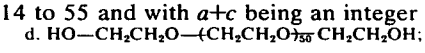
6. The photographic emulsion of claim **5**, wherein said polyalkylene oxide compound is

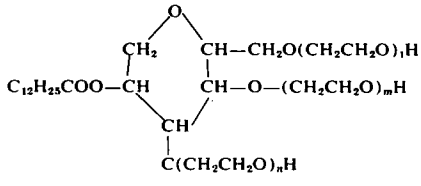
a.  ;

b.  ;

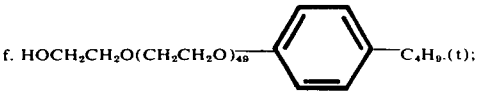
c. 

wherein *a*, *b* and *c* are integers with *b* being an integer of 14 to 55 and with *a*+*c* being an integer of 4 to 210;

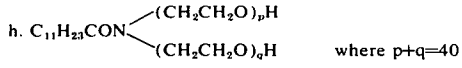
d.  ;

e. 

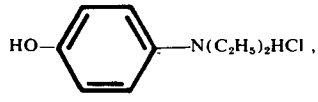
wherein 1 $+m+n$ is about 20;

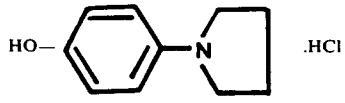
f.  ;

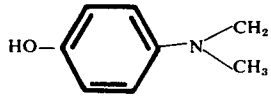
g. $C_{17}H_{35}COO(CH_2CH_2O)_{30}H$ or

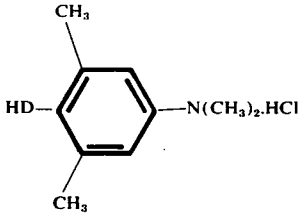
h.  where p+q=40

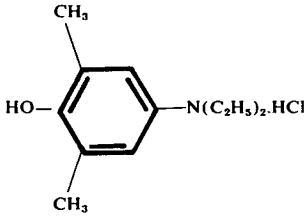
7. The photographic emulsion of claim **1**, wherein said organic compound of the general formula (I) is

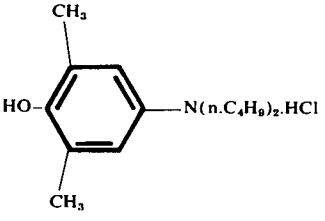
 ,

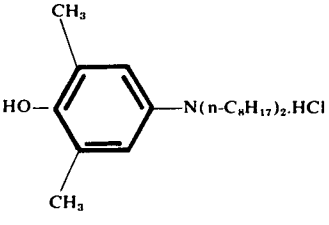
 .HCl

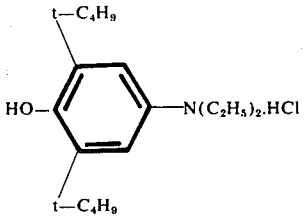
 .HCl,

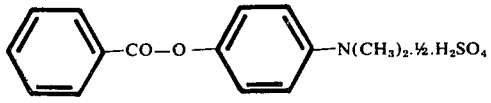
 .HCl

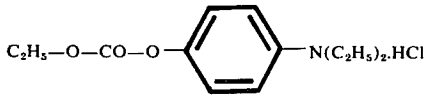
 .HCl

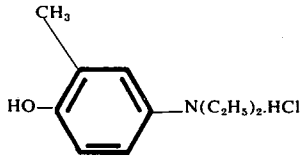
 .HCl

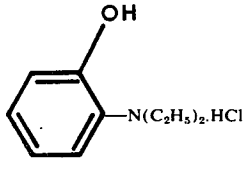
 .HCl

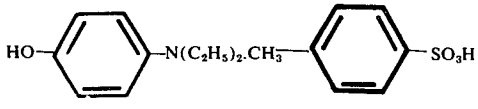


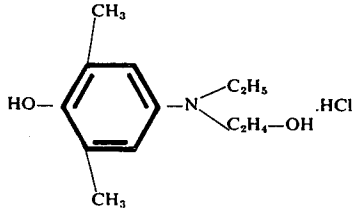


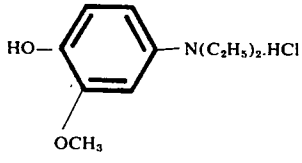


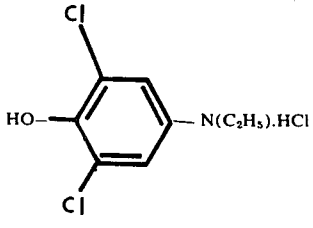


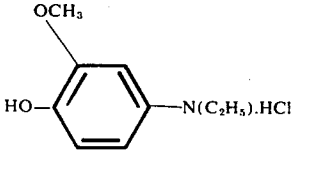




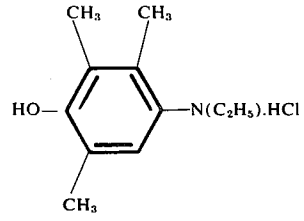




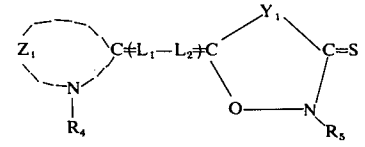




or

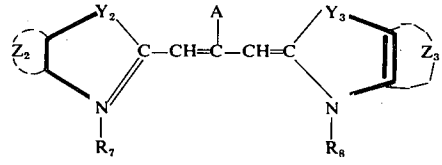


8. The photographic emulsion of claim **1**, wherein said emulsion contains at least one of a sensitizing dye of the general formula (II)



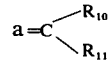
(II)

wherein Z_1 represents a group of atoms necessary for forming a heterocyclic ring; L_1 and L_2 each represents a methine chain; Y_1 represents an oxygen atom, a sulfur atom or a $=N-R_6$ group in which R_6 is an aliphatic group or an aryl group; n is an integer of 0 or 1; R_4 and R_5 are each an aliphatic group or an aryl group; and a compound of the general formula (III)



(III)

wherein A is a hydrogen atom or a lower alkyl group containing not more than **3** carbon atoms; Z_2 and Z_3 each represents a group of atoms necessary for forming a benzene or a naphthalene ring; Y_2 and Y_3 are each an oxygen atom, a sulfur atom, a selenium atom, a $=N-R_9$ group, in which R_9 is an aliphatic group, or



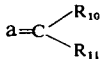
group, in which R_{10} and R_{11} are each an alkyl group; R_7 and R_8 each represents an aliphatic group; X is an anion; and p is **1** or **2**, p being 1 when the compound forms an intramolecular salt.

9. The photographic emulsion of claim **8**, wherein said Z_1 is a tetrazole ring, a pyrrolidine ring, a pyridine ring, a thiazole ring, a thiazoline ring, a selenazole ring, a selenazoline ring, an oxazole ring, an oxazoline ring, an imidazole ring, an imidazoline ring or an indolenine ring and wherein said heterocyclic ring formed Z_2 and Z_3 each is 5-phenyl-benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-methoxycarbonylbenzoxazole, 5-chlorobenzothiazole, 5-methoxybenzothiazole, 5-chloro-6-methylbenzothiazole, β-naphthothiazole, β,β'-naphthothiazole, 5-methylbenzoselenazole, benzoselenazole, 5,6-dichlorobenzimidazole, 5-trifluoromethylbenzimidazole, 5-chloro-6-methylsulfonylbenzimidazole, 5-methoxycarbonylbenzimidazole, or naphthoimidazol-1,1'-dimethylindolenine.

10. The photographic emulsion of claim **8**, wherein R_4 and R_5 each is an alkyl group, a carboxyalkyl group, a sulfoalkyl group, an allyl group, an aminoalkyl group,

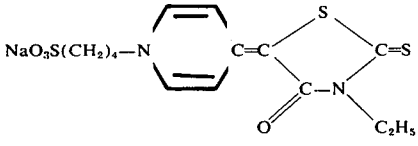
an acetoxyalkyl group, an aralkyl group or an aryl group and wherein R_7 and R_8 each is an alkyl group, an alkenyl group, a hydroxyalkyl group, an amidoalkyl group, an aralkyl group, a carboxyalkyl group or a sulfo alkyl group.

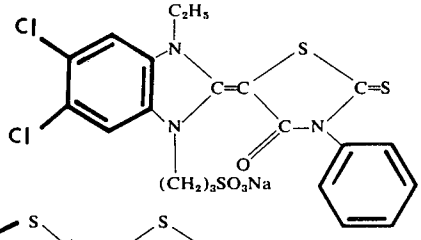
11. The photographic emulsion of claim **10,** wherein L_1 and L_2 each is a methine chain, a methyl methine chain, an ethyl methine chain, a phenyl methine chain and a 2-hydroxyethyl methin chain R_6 is an alkyl group, a cyanoalkyl group, an allyl group, carboxyalkyl group, an aminoalkyl group, an aralkyl group a hydroxyalkyl group or an aryl group; R_9 is an alkyl group, an allyl group, an acetoxyalkyl group, a cyanoalkyl group or

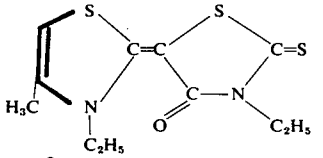


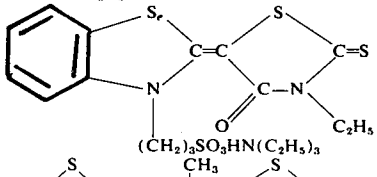
group and R_{10} and R_{11} are each an alkyl group.

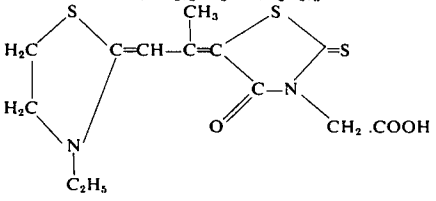
12. The photographic emulsion of claim **1,** wherein said emulsion contains at least one dye selected from the group consisting of

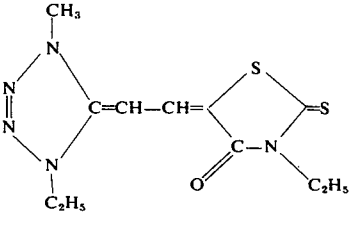


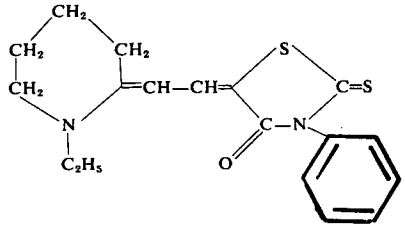


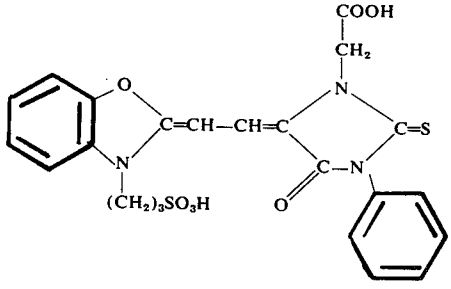


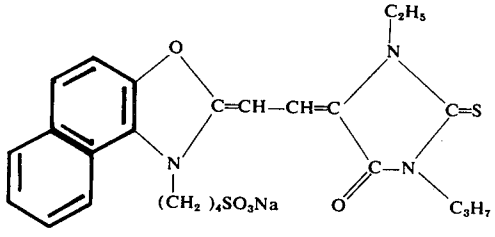


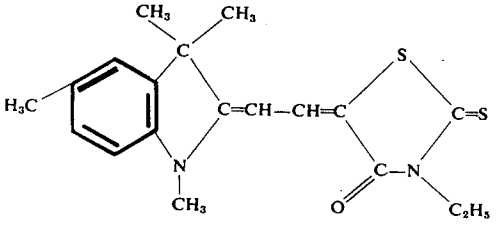


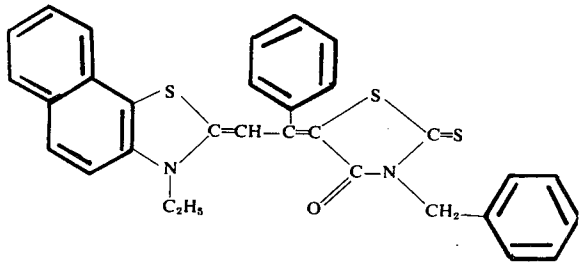


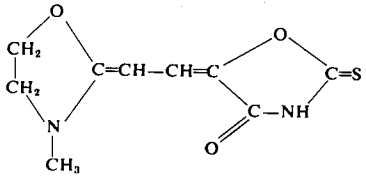


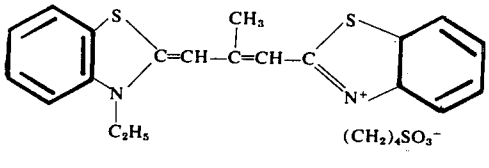


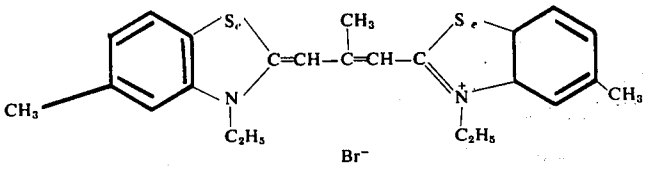


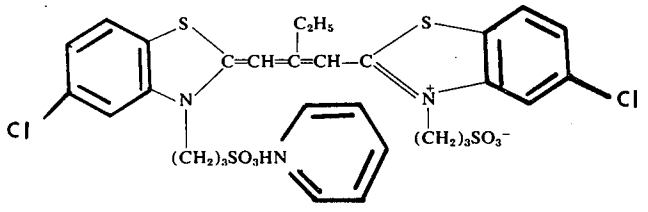


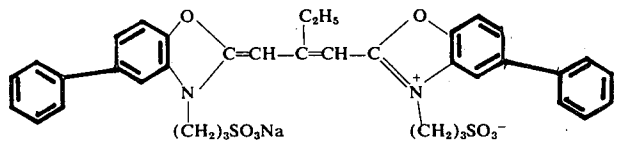


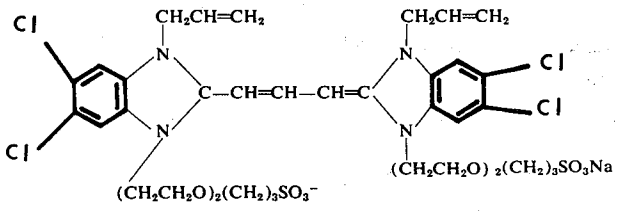


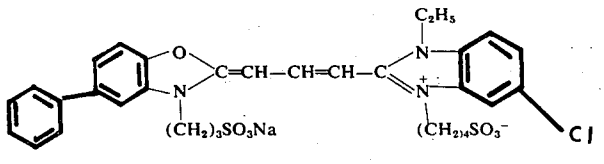


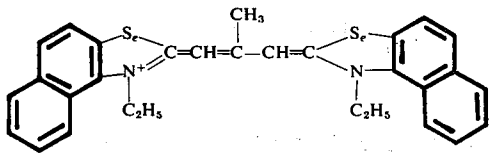


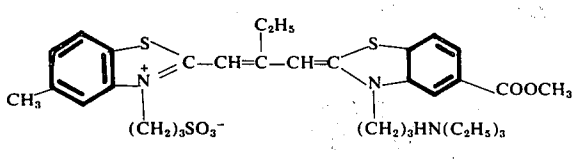


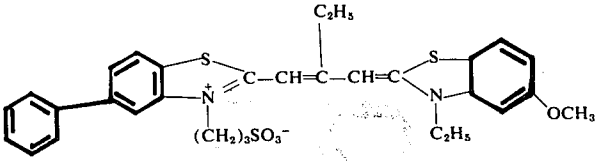


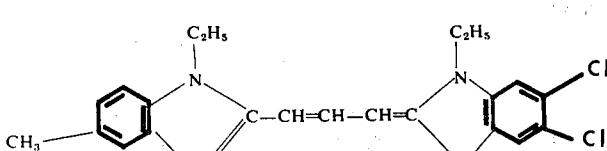












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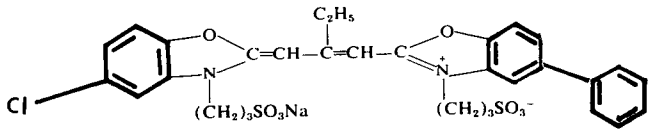
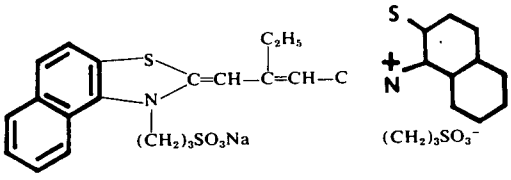
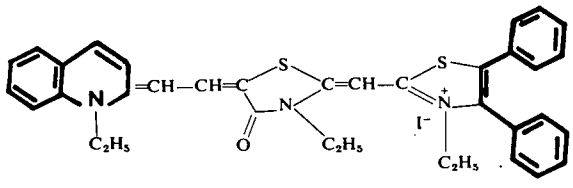
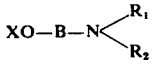






13. A silver halide photosensitive material containing as a photosensitive layer thereof the silver halide photographic emulsion as claimed in claim **1.**

14. The photographic emulsion of claim **13,** in which said organic compound has the following general formula (I-*a*)



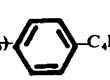
(I-a)

wherein B represents a bivalent benzene type aromatic ring group, and X, R_1 and R_2 each is as defined in claim **1.**

15. The silver halide photosensitive material of claim **13,** wherein A is a unsubstituted or substituted benzene group, naphthalene group, pyrimidine group, or triazine group, said substituents being alkyl, alkoxy, hydroxy, halogen, alkoxycarbonyl, quaternary aminoalkyl, aralkyl or aryl groups; R_1 and R_2 each is an alkyl group, an alkenyl group, an aralkyl group or an aryl group or R_1 and R_2 can combine together to form a saturated or unsaturated ring; X represents a hydrogen atom, an acyl group, or an acyloxy group.

16. The silver halide photosensitive material of claim **13,** wherein said polyalkylene oxide compound has a molecular weight ranging from about 500 to 25,000.

17. The silver halide photosensitive material of claim **16,** wherein said polyalkylene oxide compound is

a. $HO-CH_2CH_2-O+CH_2CH_2O)_{\overline{a}}$  $-C_4H_{19}$;

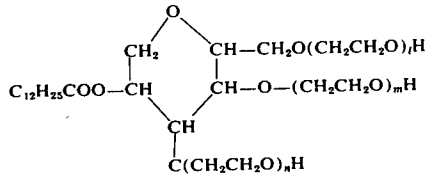
b. $HO-CH_2CH_2-O+CH_2CH_2O)_{\overline{40}}CO(CH_2)_7CH=CH-C_8H_{17}$;

c. $HO+CH_2CH_2O)_{\overline{a}}+CHCH_2O)_{\overline{b}}+CH_2CH_2O)_{\overline{c}}H$

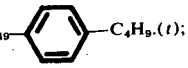
CH_3

wherein *a*, *b* and *c* are integers with *b* being an integer of **14** to **55** and with *a*+*c* being an integer of 4 to 210;

d. $HO-CH_2CH_2O+CH_2CH_2O)_{\overline{50}}CH_2CH_2OH$;



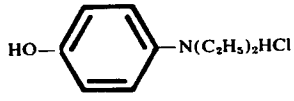
wherein *l*+*m*+*n* is about 20;

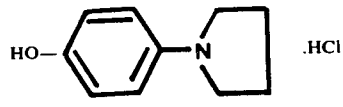
f. $HOCH_2CH_2O(CH_2CH_2)_{49}$  $-C_4H_9.(t)$;

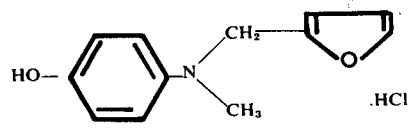
g. $C_{17}H_{35}COO(CH_2CH_2O)_{30}H$ or

h. $C_{11}H_{23}CON<^{(CH_2CH_2)_pH}_{(CH_2CH_2O)_qH}$

18. The silver halide photosensitive material of claim **13,** wherein said organic compound of the general formula (I) is







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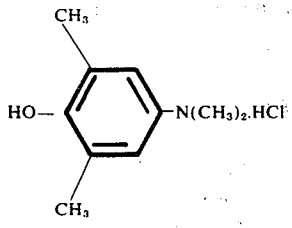

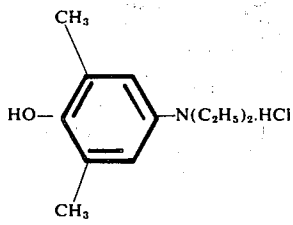

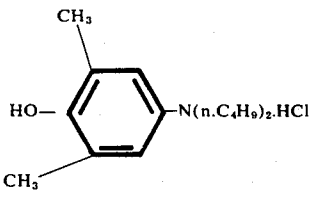

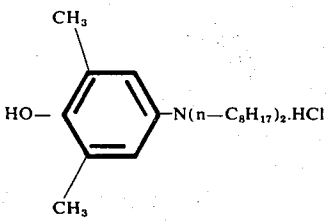

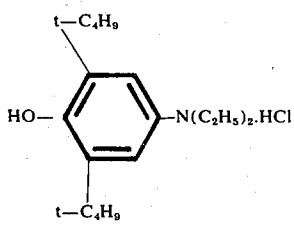

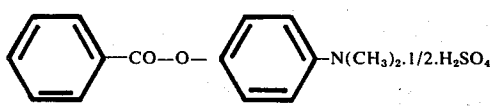

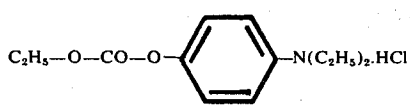

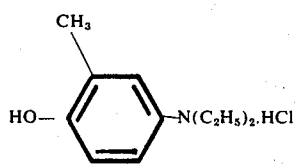

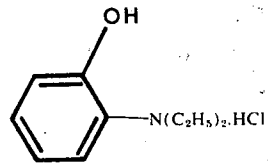

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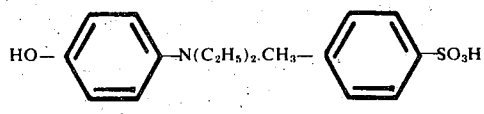
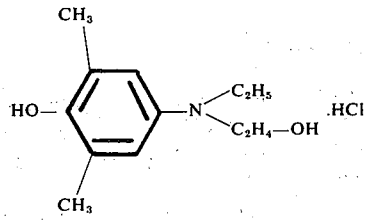
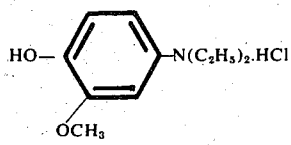
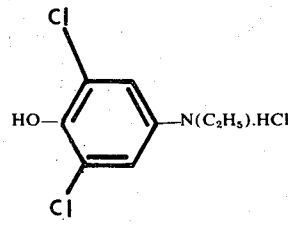
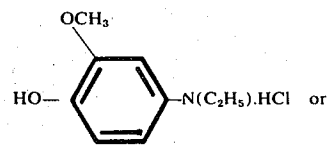
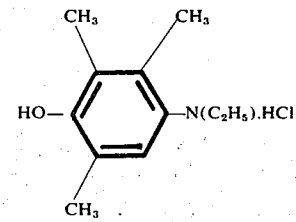




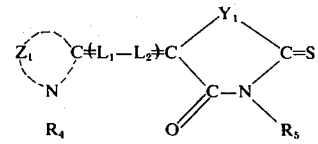






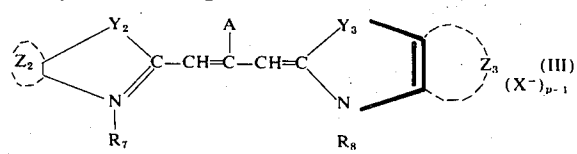


19. The silver halide photosensitive material of claim **13,** wherein said emulsion contains at least one of a sensitizing dye of the general formula (II)



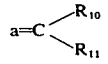
(II)

wherein Z_1 represents a group of atoms necessary for forming heterocyclic ring; L_1 and L_2 each represents a methine chain; Y_1 represents an oxygen atom, a sulfur atom or a $=N-R_6$ group in which R_6 is an aliphatic group or an aryl group; n is an integer of 0 or 1; R_4 and R_5 are each an aliphatic group or an aryl group and a compound of the general formula (III)



(III)

wherein A is a hydrogen atom or a lower alkyl group containing not more than 3 carbon atoms; Z_2 and Z_3 each represents a group of atoms necessary for forming a benzene or a naphthalene ring; Y_2 and Y_3 are each an oxygen atom, a sulfur atom, a selenium atom, a $=N-R_9$ group, in which R_9 is an aliphatic group, or



group, in which R_{10} and R_{11} are each an alkyl group; R_7 and R_8 each represents an aliphatic group; X is an anion; and p is 1 or 2, p being 1 when the compound forms an intramolecular salt.

20. A phototypesetting material containing the silver halide photographic emulsion as claimed in claim **3.**

21. The phototypesetting material of claim **20** wherein R_1 and R_2 each is an alkyl group, an alkenyl group, an aralkyl group or an aryl group or R_1 and R_2 can combine together to form a saturated or unsaturated ring; X represents a hydrogen atoms, an acyl group, or an acyloxy group.

22. The phototypesetting material of claim **20,** wherein said polyalkylene oxide compound has a molecular weight ranging from about 500 to 25,000.

23. The phototypesetting material of claim **22,** wherein said polyalkylene oxide compound is

a. $HO-CH_2CH_2-O+CH_2CH_2O)_{30}-C_4H_{19}$;

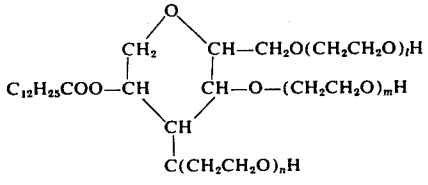
b. $HO-CH_2CH_2O-CH_2CH_2O+_{40}CO(CH_2)_7CH=CH-C_8H_{17}$;

c. $HO+CH_2CH_2O)_a+CHCH_2O)_b+CH_2CH_2O)_cH$

CH_3

wherein a, b and c are integers with b being an integer of 14 to 55 and with $a+c$ being an integer of 4 to 210;

d. $HO-CH_2CH_2O(CH_2CH_2O)_{50}CH_2CH_2OH$;



wherein $l+m+n$ is about 20;

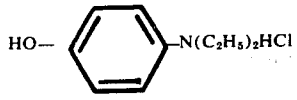
f. $HOCH_2CH_2O(CH_2CH_2O)_{40}-C_4H_9.(t)$;

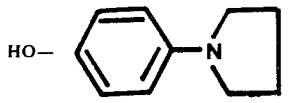
g. $C_{17}H_{35}COO(CH_2CH_2O)_{30}H$ or

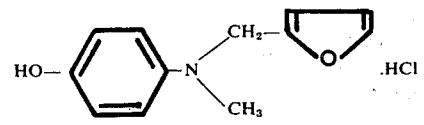
h. $C_{11}H_{23}CON<^{(CH_2CH_2O)_pH}_{(CH_2CH_2O)_qH}$

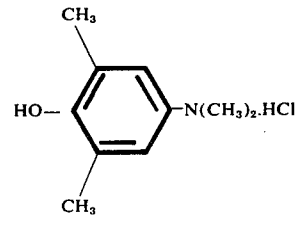
where p+q=40

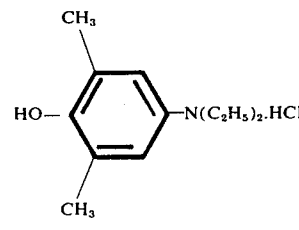
24. The phototypesetting material of claim **23,** wherein said organic compound of the general formula (I) is

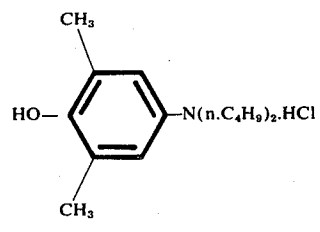


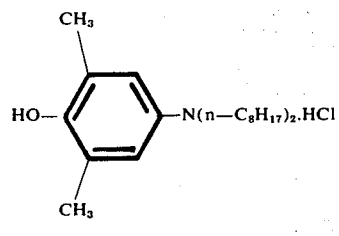


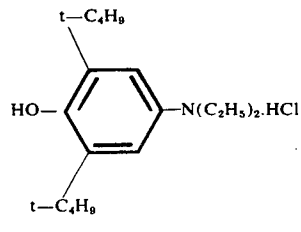


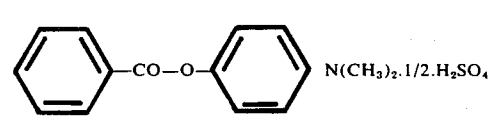


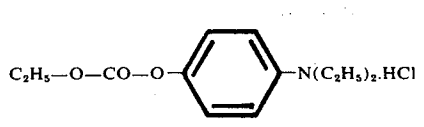












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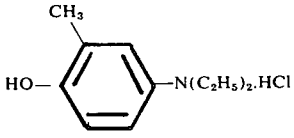
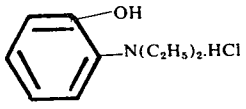
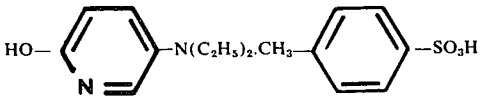
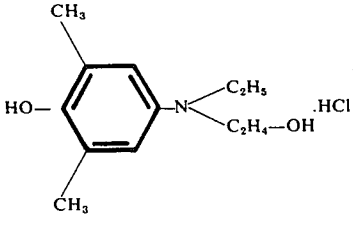
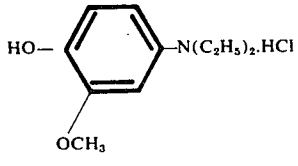
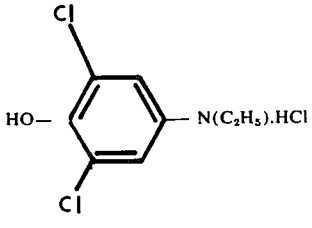


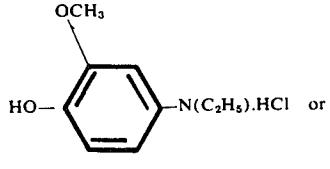


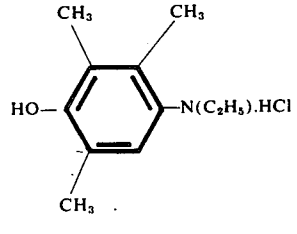




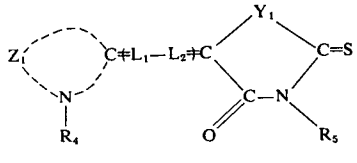






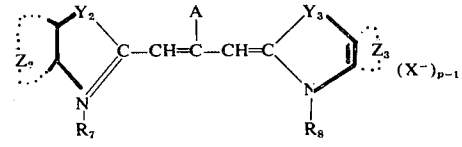


25. The phototypesetting material of claim **20**, wherein said emulsion contains at least one of a sensitizing dye of the general formula (II)



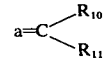
(II)

wherein Z_1 represents a group of atoms necessary for forming heterocyclic ring; L_1 and L_2 each represents a methine chain; Y_1 represents an oxygen atom, a sulfur atom or a $=N-R_6$ group in which R_6 is an aliphatic group or an aryl group; n is an integer of 0 or 1; R_4 and R_5 are each an aliphatic group or an aryl group; and a compound of the general formula (III)



(III)

wherein A is a hydrogen atom or a lower alkyl group containing not more than 3 carbon atoms; Z_2 and Z_3 each represents a group of atoms necessary for forming a benzene or a naphthalene ring; Y_2 and Y_3 are each an oxygen atom, a sulfur atom, a selenium atom, a $=N-R_9$ group, in which R_9 is an aliphatic group, or



group, in which R_{10} and R_{11} are each an alkyl group; R_7 and R_8 each represents an aliphatic group; X is an anion; and p is 1 or 2, p being 1 when the compound forms an intramolecular salt.

26. The emulsion of claim **1** wherein said OX-group is in the position ortho to said N-atom.

27. The emulsion of claim **1** wherein said OX-group is in the position para to said N-atom.

28. The emulsion of claim **1** wherein X is hydrogen.

29. The emulsion of claim **1** wherein X is a group capable of being dissociated therefrom with an inorganic or organic base.

30. The emulsion of claim **4** wherein A is said benzene group.

31. The emulsion of claim **4** wherein A is said naphthalene group.

32. The emulsion of claim **4** wherein A is said pyrimidine group.

33. The emulsion of claim **4** wherein A is said triazene group.

34. The silver halide photosensitive material of claim **13** wherein said OX-group is in the position ortho to said N-atom.

35. The silver halide photosensitive material of claim **13** wherein said OX-group is in the position para to said N-atom.

36. The silver halide photosensitive material of claim **13** wherein X is hydrogen.

37. The silver halide photosensitive material of claim **13** wherein X is a group capable of being dissociated therefrom with an inorganic or organic base.

38. The silver halide photosensitive material of claim **15** wherein A is said benzene group.

39. The silver halide photosensitive material of claim **15** wherein A is said naphthalene group.

40. The silver halide photosensitive material of claim 15 wherein A is said pyrimidine group.

41. The silver halide photosensitive material of claim 15 wherein A is said triazene group.

42. The phototypesetting material of claim 20 wherein said OX-group is in the position ortho to said N-atom.

43. The phototypesetting material of claim 20 wherein said OX-group is in the position para to said N-atom.

44. The phototypesetting material of claim 20 wherein X is hydrogen.

45. The phototypesetting material of claim 20 wherein X is a group capable of being dissociated therefrom with an inorganic or organic base.

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